The removal of halogens from aromatic compounds during the reduction of two activating nitro groups is a well-known phenomenon. Thus the reduction of 2,4-dibromo-3,5-dinitrotoluene with tin and hydrochloric acid gives 3,5-diaminotoluene.[3]

In contrast to the nitration with mixed acid as described above, nitration with 70% nitric acid alone according to the method of Mayes and Turner[4] led to a mixture of products from which a considerable amount of 1-nitro-4-bromobenzene was isolated. The other products were not identified.

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(3) W. A. Davis, *J. Chem. Soc.*, **81**, 873 (1902).

(4) H. A. Mayes and E. E. Turner, *ibid.*, 500 (1929).

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The Acylation of Thiophene and Furan by Means of Boron Trifluoride[1]

BY HOWARD D. HARTOUGH AND ALVIN I. KOSAK[2]

The acetylation of thiophene and furan to form the respective 2-acyl derivatives has been effected previously by means of several catalysts.[3] This reaction has now been effected by means of catalytic amounts of boron trifluoride complexes in ether, methanol, and acetic acid. The yields were satisfactory (70%) with 0.03–0.075 mole of the catalyst per mole of acetic anhydride. When acetyl chloride was used instead of acetic anhydride the yield was poor. The analogous reaction with benzoyl chloride was effected in 22% yield.

Although the nucleus of 2-acetylthiophene is acetylated in the presence of zinc chloride, orthophosphoric acid and phosphorus pentoxide,[3] acetylation at the side chain of this ketone occurred in the presence of a molecular equivalent of boron trifluoride to form a triacetylthiophene in 17% yield; however, the product has not been identified. Acetylation at the side chain might have been anticipated from the work of Meerwein, Pannwitz and Vossen[4] and Hauser and Adams.[5]

With furan, acetic anhydride and a catalytic amount of boron trifluoride in methanol, 2-acetylfuran was obtained in 46% yield.

Boron Trifluoride Complexes.—The boron trifluoride etherate was used as received from the Eastman Kodak Co. The boron trifluoride methanol complex and the boron trifluoride acetic acid complex were prepared by saturating methanol and acetic acid with boron trifluoride gas at 100 p. s. i. pressure in a stirring autoclave.

2-Acetylthiophene.—To a mixture of 252 g. (3 moles) of thiophene and 107 g. (1 mole) of 95% acetic anhydride cooled to 10° by means of an ice-bath was added 4 g. of boron trifluoride–methanol complex (60% boron trifluoride). The temperature rose to 13° and when it finally subsided after five minutes to 5° the ice-bath was removed and the flask warmed to 50° for two hours. Two hundred milliliters of water was added, the mixture agitated for fifteen minutes, the lower organic layer drawn off, washed with 10% sodium carbonate solution until neutral, and distilled. Thiophene, 180 g., was recovered and 84 g. (70%) of 2-acetylthiophene, b. p. 87–88° (8 mm.),[6] $n^{20}\mathrm{D}$ 1.5666, was obtained.

2-Benzoylthiophene.—To 126 g. (1.5 moles) of thiophene and 141 g. (1 mole) of benzoyl chloride was added 4 g. of boron trifluoride–acetic acid complex. No heat of reaction was noted and the mixture was heated at 90–95° for six hours. After cooling, the reaction mixture was washed with 10% sodium hydroxide solution until neutral. Distillation yielded thiophene, 42 g. (22%) of 2-benzoylthiophene, b. p. 146–147° (5 mm.), m. p. 56.5–57°,[7] after recrystallization from ASTM naphtha, and 21 g. of tarry residue.

"2-Triacetylthiophene."—To 42 g. (0.33 mole) of 2-acetylthiophene was added 107 g. (1 mole) of 95% acetic anhydride and 110 g. (0.84 mole) of boron trifluoride etherate. The temperature rose to 38° and after fifteen minutes the mixture was warmed on a steam-bath at 55° for thirty minutes. The hot mixture was poured slowly into one liter of water containing 120 g. of sodium acetate and shaken until the oily liquid crystallized. The crystals were filtered, washed with cold benzene, and purified by vacuum sublimation, yielding 12 g. (17%) of bright yellow crystals, m. p. 176–177°.[8]

Anal. Calcd. for $C_{10}H_{10}O_3S$: S, 15.31, Found: S, 14.92.

Oxidation with alkaline permanganate gave 2-thiophenecarboxylic acid, m. p. and mixed m. p. 127–128.5°.

2-Acetylfuran.—A procedure, analogous to that employed for to 2-acetylthiophene, was used but the temperature of the reaction mixture was maintained at 25° instead of 50° for two hours. Distillation yielded 53 g. (48%) of 2-acetylfuran, b. p. 89–90° (43 mm.),[9] m. p. 30–32°,[9] $n^{30}\mathrm{D}$ 1.5015.

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(1) Paper VII of this series.

(2) Present address: Ohio State University, Columbus, Ohio.

(3) (a) Hartough and Kosak, THIS JOURNAL, **68**, 2639 (1946); (b) **69**, 1012 (1947); (c) **69**, 3093 (1947); (d) **69**, 3098 (1947); (e) Hartough, Kosak and Sardella, *ibid.*, **69**, 1014 (1947); (f) Hartough and Conley, *ibid.*, **69**, 3096 (1947).

(4) Meerwein, *Ber.*, **66B**, 411 (1933); Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934); Meerwein and Vossen, *ibid.*, **141**, 149 (1934).

(5) Hauser and Adams, THIS JOURNAL, **66**, 345 (1944).

(6) Reported data (ref. 3a): b. p. 77–78° (4 mm.) and $n^{20}\mathrm{D}$ 1.5666.

(7) Reported data (ref. 3b); b. p. 143–144 (4 mm.) and m. p. 56.5–57°.

(8) Alternate purification procedures involved numerous recrystallizations from benzene or precipitation of the material from ethyl acetate by addition of petroleum ether yielding brown crystals, m. p. 173–175°.

(9) Reported data (ref. 3c): m. p. 30–32° and b. p. 45–50° (5 mm.).

SOCONY-VACUUM LABORATORIES
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Derivatives of Diethylamino Compounds

BY NELSON J. LEONARD, FELICE MARY KRAFT AND VIVIAN WOLFMAN

In connection with studies in progress on reactions of aminoalcohols and aminoketones involving possible rearrangement, it was desirable to obtain readily identifiable derivatives of certain diethylamino compounds. The compounds of interest included amines, aminoethers, aminoalcohols and aminoketones, in all of which the amine function was tertiary. Derivatives have been formed with picric acid, picrolonic acid and ethyl iodide. Diethyl-*n*-propylamine has been obtained